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U.S. Department of Agriculture, U.S. Forest Service
Pacific Northwest Region
Portland, Oregon

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PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

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ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

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SUMMARY

On February 11, 1998, the National Institute for Occupational Safety and Health (NIOSH) received a request for a health hazard evaluation (HHE) from the U.S. Forest Service (USFS) to evaluate and compare Forestry Technicians' (timber markers) exposures to a newly-formulated waterborne tree marking paint. In a previous NIOSH investigation (HHE 93-1035-2686) Foresters reported respiratory irritation, nausea, vomiting, and central nervous system (CNS) symptoms including headaches, dizziness, and fatigue when using alkyd enamel tree marking paint. Results from the previous HHE revealed total hydrocarbon exposures from trace concentrations to 6.3 milligrams per cubic meter (mg/m^3). Biological monitoring results revealed that methyl ethyl ketone (MEK) was detectable in urine samples but all samples were below the biological exposure index of 2 milligrams of MEK per liter of urine. All exposures were below the Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs) for solvents, metals, and dusts. NIOSH concluded that the health effects reported were likely to be caused by chronic low-level exposures to mixed solvents. To reduce solvent exposures, NIOSH recommended the Forest Service use a high solid, low solvent, waterborne paint such as an acrylic latex enamel. The results of this study show that when employees used the waterborne paint formulation, exposures to total hydrocarbons were either below the limit of detection or were at trace concentrations (see Appendix A). Propylene glycol was the only chemical detected in quantitative amounts in 3 of 12 samples, in a range of 0.10 to 0.35 parts per million (ppm). Methyl ethyl ketone (MEK) was detected in low concentrations in most employee urine samples collected in the previous investigations but was below the limit of detection in all (15 samples) of the urine samples collected in this investigation. The USFS requested NIOSH's assistance in developing a formulation list for waterborne paint and is in the final stages of developing specifications for manufacturers to bid on contracts to manufacture the new paint (see Appendix A).

An occupational health hazard was not determined for U.S. Forest Service Foresters who marked timber during this investigation using waterborne paint. Employees did not report irritant or CNS effects and solvent exposures were mostly below the limit of detections for total hydrocarbons (referenced as stoddard solvent), toluene, trimethyl benzene, methyl isobutyl ketone, propylene glycol, 2-butoxyethanol, and methyl ethyl ketone. Biological monitoring results (urine) were all below the limits of detection for propylene glycol, methyl ethyl ketone, methyl isobutyl ketone, and 2-butoxyethanol. Substitution of stoddard solvent-based, alkyd enamel with a propylene glycol-based waterborne paint is the primary intervention identified in this HHE responsible for reduced solvent exposure and dose and reduced health complaints in Foresters using waterborne paint.

Keywords: Foresters, Forestry Technicians, tree marking paint, enamel, waterborne paint, solvents, hydrocarbons, propylene glycol, methyl ethyl ketone, MEK, methyl isobutyl ketone, MIBK, butyl cellosolve, 2-butoxyethanol

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INTRODUCTION

On February 11, 1998, the U.S. Forest Service (USFS) requested that a representative of NIOSH conduct a health hazard evaluation (HHE) to evaluate and compare timber marker's (also called Forestry Technicians) exposures to a new waterborne formulation of tree marking paint developed for use by the U.S. Forest Service. NIOSH performed several previous investigations to document Forestry Technicians' exposures to alkyd enamel tree marking paint traditionally used by the USFS for timber marking operations. On May 18, 1998, two NIOSH industrial hygienists met with USFS employees and management representatives in LaGrande, Oregon, where an opening conference was conducted to discuss details of this investigation which occurred May 19–21, 1998, at the Little Bear timber sale in the Catherine Creek Wildlife Unit located approximately 25 miles southeast of LaGrande.

BACKGROUND

USFS Forestry Technicians who select and mark timber were the subject and focus of this HHE. Forestry Technicians work in teams, usually four to six individuals who enter a designated stand of timber and systematically mark timber using hand-held paint guns to mark trees either to cut or to leave based upon the size, height, and condition of the tree. Trees are marked using a proprietary paint formulated to USFS specifications and which meets the qualified product list. Foresters generally apply tree marking paint on two locations: (1) a mark on the tree trunk at approximately three feet (to mark what will eventually become the log), and: (2) just above ground level (what will eventually be the stump). Marks made by Foresters vary with the individual and may range from a stripe, a blaze mark such as an X or a Y shaped mark, to a solid circle or dot.

Paints can be applied by means of pressurized aerosol spray cans or squirted on the tree with

mechanical paint guns. Both paint delivery systems present opportunities for worker exposures. The aerosol systems emit a fine mist of paint that can be influenced by wind conditions that blow paint mists into (or away) from the breathing zones of the workers. In contrast, the mechanical paint guns deliver a denser stream of paint which produces less visible aerosol, and is less likely to be influenced by the wind. However, the paint stream can splatter back from the irregular surface of the bark onto the worker's clothes (which can result in dermal exposures) and can create aerosols which can be inhaled. The paint gun tip can clog and must be taken apart periodically and cleaned. Removal of the applicator tip can contaminate work gloves, which can also result in dermal exposures. On occasion, paint aerosol is visible in the air. Solvent odor can also be noticed depending on the type of paint used, the number of Foresters working in a given area, terrain type, elevation, ambient air temperature, relative humidity (RH), wind direction, and wind speed.

Foresters working on tree marking crews are expected to wear personal protective equipment (PPE). Each employee is supplied with rain gear, hard hat, goggles or safety glasses, cotton and leather gloves, and sturdy leather boots. Disposable dust masks are also available. Weather conditions and worker comfort tend to influence the degree to which workers comply with PPE policies. Workers report that complete protective gear is least likely to be worn during the warmer summer season.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though

their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),¹ (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®),² and (3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs).³ NIOSH encourages employers to follow the OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criterion. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8-to-10-hour workday. Some substances have recommended short-term exposure limits (STEL), or ceiling values, which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

Propylene glycol

Propylene glycol is a liquid substance that absorbs water. Propylene glycol can be used to make antifreeze for automobiles and is in wide use in the chemical and pharmaceutical industries as a material to absorb water in foods, medicines, and cosmetic products. Propylene glycol is a colorless, odorless, clear liquid at room temperatures and can be present as a vapor in the air. Propylene glycol can be absorbed through the skin. The widespread use of propylene glycol in foods and cosmetics is due to its low toxicity. Propylene glycol has a low toxicity in humans because it can be quickly excreted unchanged (or biotransformed as a simple conjugate) by human metabolism.⁴ No deaths have been reported as a result of exposures to propylene glycol.⁴ No OSHA, NIOSH, or ACGIH health criteria exist for occupational exposure to propylene glycol.

Methyl Ethyl Ketone

Methyl ethyl ketone (MEK) is a colorless, flammable organic solvent with a characteristic odor similar to acetone and is typically used as a solvent in the surface coating and synthetic resin industries.⁵ MEK is absorbed primarily through inhalation and causes irritation of the eyes, mucous membranes, and skin; at high concentrations MEK may cause central nervous system depression. Short duration inhalation exposure to 100 parts per million (ppm) of MEK was reported to cause slight nose and throat irritation, 200 ppm caused mild eye irritation, and 300 ppm was associated with headaches, throat irritation, as well as an objectionable odor.⁶ Additional studies indicate that MEK by itself does not cause neurologic toxicity of the extremities (peripheral neuropathy), but may potentiate the toxic effects of substances known to cause peripheral neuropathy, such as n-hexane.^{7,8} Continued or prolonged skin contact with MEK liquid can cause dermatitis.

The National Toxicology Program, an interagency research program, has not found evidence supporting

an association between MEK exposure and the development of cancer in humans or experimental animals.⁹ NIOSH, OSHA, and ACGIH have proposed the same full-shift inhalation criteria for MEK at 200 ppm averaged over an 8-hour exposure and a STEL of 300 ppm for 15 minutes.

Toluene

Toluene is a colorless, aromatic organic liquid containing a six carbon ring (a benzene ring) with a methyl group (CH₃) substitution. It is a typical solvent found in paints and other coatings, and used as a raw material in the synthesis of organic chemicals, dyes, detergents, and pharmaceuticals. It is also an ingredient of gasoline, ranged from 5% to 22%. A previous NIOSH evaluation found the toluene content of gasoline ranging from 2.4% to 12%, with exposure levels from none detected to 2.1 milligrams per cubic meter (mg/m³) (0.56 ppm).¹⁰

Inhalation and skin absorption are the major occupational routes of entry. Toluene can cause acute irritation of the eyes, respiratory tract, and skin. Since it is a defatting solvent, repeated or prolonged skin contact will remove the natural lipids from the skin which can cause drying, fissuring, and dermatitis.^{11,12}

The main effects reported with excessive inhalation exposure to toluene are central nervous system (CNS) depression and neurotoxicity.¹² Studies have shown that subjects exposed to 100 ppm of toluene for six hours complained of eye and nose irritation, and in some cases, headache, dizziness, and a feeling of intoxication (narcosis).^{13,14,15} No symptoms were noted below 376 mg/m³ (100 ppm) in these studies. There are a number of reports of neurological damage due to deliberate sniffing of toluene-based glues resulting in motor weakness, intention tremor, ataxia, as well as cerebellar and cerebral atrophy.¹⁶ Recovery is complete following infrequent episodes, however, permanent impairment may occur after repeated and prolonged glue-sniffing abuse. Exposure to extremely high concentrations of toluene may cause mental

confusion, loss of coordination, and unconsciousness.^{17,18}

Originally, there was a concern that toluene exposures produced hematopoietic toxicity because of the benzene ring present in the molecular structure of toluene. However, toluene does not produce the severe injury to bone marrow characteristic of benzene exposure as early reports suggested. It is now believed that simultaneous exposure to benzene (present as a contaminant in the toluene) was responsible for the observed toxicity.^{11,17}

The NIOSH REL for toluene is 100 ppm for an 8-hour TWA.¹ NIOSH has also set a recommended STEL of 150 ppm for a 15-minute sampling period. The OSHA PEL for toluene is 200 ppm for an 8-hour TWA.³ The recently adopted ACGIH TLV is 50 ppm for an 8-hour exposure level.² This ACGIH TLV carries a skin notation, indicating that cutaneous exposure contributes to the overall absorbed inhalation dose and potential systemic effects.

2-Butoxyethanol

2-Butoxyethanol, also known as ethylene glycol monobutyl ether, or butyl Cellosolve®, is a colorless liquid solvent with a reported odor threshold of 0.1 ppm where the chemical has a mild ether-like smell.¹⁹ 2-butoxyethanol is a widely used solvent and cleaning agent. Toxic effects associated with human exposure to 2-butoxyethanol include eye and nasal irritation, headache, vomiting, and altered taste.^{20,21} The material is harmful if inhaled, ingested, or absorbed through the skin. Animal studies have demonstrated that 2-butoxyethanol is a hemolytic agent, and has caused blood changes in the animals studied.¹⁸ This effect appears to be more pronounced in animals than humans. The low vapor pressure of 2-butoxyethanol (0.88 mm Hg) is such that high air concentrations are unlikely, however, the material can be absorbed through the skin. The NIOSH REL for 2-butoxyethanol is 5 ppm as a 10-hour TWA.¹

MATERIALS AND METHODS

Six Foresters participated in the HHE. On the morning of the first day, voluntary consent forms were given to everyone to read and sign. The consent form acknowledged the employees' permission for NIOSH to collect and analyze employee urine samples for specific solvents confirmed to be present in the marking paint. Employees were individually notified of results of urine sample analysis by letters which were sent directly from NIOSH to the employees' home addresses, which had been provided by the employees.

Bulk samples (approximately 20 cubic centimeters) of Niles brand waterborne tree marking paint were sent to NIOSH by the USFS for analyses. NIOSH laboratories used head space and gas chromatography/mass spectroscopy analyses to determine volatile paint constituents. Paint was extracted in separate analyses using carbon disulfide and methanol. The extracts were filtered and analyzed by gas chromatography and mass spectrometry (GC-MS). Additionally, headspace samples were collected above portions of bulk paint using thermal desorption tubes. The air samples were collected for a period of 15 minutes at a flow rate of 50 cc/minute. Samples were analyzed using a Perkin-Elmer ATD 400 automatic thermal desorption system which interfaced directly with a GC-MS. Based on these analyses, NIOSH developed a sampling protocol to evaluate Foresters' exposures to propylene glycol, 2-butoxyethanol (butyl cellosolve) methyl ethyl ketone (2-butanone) and methyl isobutyl ketone (MIBK), total hydrocarbons (as stoddard solvent), toluene, and all isomers of trimethyl benzene (TMB). Air sampling trains were calibrated using a primary standard at LaGrande, Oregon (elevation 2872 feet above sea level). Due to the barometric pressure difference between LaGrande, where the sampling trains were calibrated, and the timber sale where sampling was performed (elevation 5137 feet above sea level), an

air density correction factor was calculated and used in determining correct air sample volumes.

Foresters were asked to wear four air sampling trains to obtain personal breathing zone (PBZ) exposures. One sampling train collected total hydrocarbons, toluene, TMB, and MIBK. Another sampling train collected MEK, a third sampling train collected propylene glycol, and a fourth train collected 2-butoxy ethanol. Two sampling media were attached on the right and left sides of the employees' lapels or the field vests. Sampling media and the sampling pumps were checked several times in the morning and afternoon periods of work. NIOSH industrial hygienists accompanied the employees in the field each day to observe employee work practices and techniques, discuss work practices with the employees, and to perform periodic flow checks on the air sampling trains.

A total of 48 PBZ samples were collected using either SKC® pocket pumps or Gilian® low-flow pumps configured with the sampling media connected in-line with Tygon® tubing. Total hydrocarbons and 2-butoxyethanol were each collected separately using coconut-shell charcoal solid sorbent tubes (100 milligrams [mg]/50 mg) with each sampling train calibrated to a flow rate of 100 milliliters per minute (mL/min). Propylene glycol was collected on OVS 7® tubes containing XAD 7 beaded sorbent at a flow rate of 100 mL/min. MEK was collected using beaded carbon (Anasorb 747®) sorbent tubes at a flow of 100 mL/min. To characterize VOC emissions directly after tree marking paint had been applied to timber, thermal desorption tubes were used to collect two air samples at 50 cc/min. The thermal desorption sampling media were analyzed in-house by NIOSH using GC/MS, using a Perkin-Elmer ATD 400 thermal desorption system.

Pre- and post-shift urine samples were collected for biological monitoring. Employees were requested to provide urine samples. Urine samples were analyzed for the presence of propylene glycol, MEK, MIBK, and 2-butoxyacetic acid. Urine was collected and immediately transferred to the brim of

a labeled specimen vial (to restrict headspace and to prevent any loss from volatilization), immediately refrigerated, and shipped overnight to a NIOSH contract toxicology laboratory. The laboratory was requested to hold analysis on the pre-shift samples until all post-shift samples were analyzed. If any of the post-shift samples had solvents or solvent metabolites present above the limit of detection, the laboratory was instructed to analyze the pre-shift samples. In the event all post-shift samples were found to be below the limit of detection for metabolites or individual solvents, pre-shift samples were not analyzed and the laboratory was directed to dispose of the samples. Splits of urine samples were labeled and shipped with each days samples for use as blind laboratory control samples.

FIELD OBSERVATIONS

Two teams of three Foresters marked timber over three consecutive days. Timber consisted of a mixed coniferous forest of Douglas fir, white fir, tamarack (western larch), and Ponderosa pine. Niles brand blue waterborne tree marking paint was the only paint used during this survey. Foresters' used Nelspot and Trecoder brand paint guns to apply the paint.

Weather varied from moderate temperatures and intermittent periods of sun and overcast skies to periods of rain, and mixed snow and rain on the last day of the investigation. Temperatures at the site ranged from 40–50°F in the morning to a high of 64–70°F in the afternoons of the first two days of the survey. RH was measured in a range of 50–54% in the mornings to 42–45% in the afternoons. The highest humidity and coldest temperatures occurred on the last day of the survey when temperatures varied from 32–40°F and up to 74% RH. Winds varied from not detectable in the early morning to 1–2 miles per hour (mph) during the afternoon.

As observed during the four previous investigations, NIOSH industrial hygienists noted that timber-marking techniques varied somewhat between Foresters. Some employees spray a

minimal amount of paint, while others apply more paint to each tree. Some Foresters used three squirts of paint to mark a tree and others used four or more squirts to mark a particular tree. Some employees first apply the stump dot, then mark the breast blaze, while others apply the breast blaze first then the stump dot. For example, during this investigation one technician used a ✓ mark which required two squirts of paint to mark the trunk, another used an X mark, requiring two trigger pulls; another simply used a vertical line, which used one, occasionally two squirts of paint. Compared to the alkyd enamel paints evaluated on the Wallowa–Whitman National Forest in July 1997, less paint splatter was observed during this investigation. Solvent odor which was frequently apparent during tree marking during the July 1997, investigation was not commonly noted during this survey.

RESULTS

NIOSH analysis of bulk paint samples revealed the presence of more than 35 chemicals either in the headspace analysis (the air immediately above a sample of paint), or by direct GC–MS analysis of the paint. The major compounds detected (in order of preponderance) were propylene glycol, butyl cellosolve, and a hydrocarbon mixture of primarily C₉–C₁₂ alkanes plus some alkyl benzenes (such as trimethyl benzenes). Compounds identified in the headspace analysis included methanol, (much greater amounts in orange paint compared to blue) MEK, MIBK, methyl propyl ketone, toluene, hexanal, xylene, propylene glycol methyl ether acetate, butyl acetate, methyl amyl ketone, and 2–methyl–2–propanol.

The material safety data sheet for Niles brand blue water cleanup listed the following materials (all materials as a percentage by weight): propylene glycol (1,2, dihydroxypropane) 31%, silicates 4%, mineral spirits 3%, and odorless mineral spirits 2%.

Twelve of the PBZ samples were collected for total hydrocarbons, toluene, TMB, and MIBK. Toluene, TMB, and MIBK were not detected (ND) to the

limits of detection (LOD) 0.0003 mg/sample for toluene and 0.0004 mg/sample for both TMB and MIBK. Three of 12 samples (25%) had trace concentrations (at or between the LOD and limit of quantitation [LOQ]) of total hydrocarbons (referenced as stoddard solvent). NIOSH considers concentrations between the LODs and LOQs to be trace or non numerical concentrations.

Of 12 PBZ samples collected for propylene glycol, 9 (75%) of the samples revealed trace concentrations. Three samples (25%) were reported above the LOQ of 0.01 mg/sample and were in range of 0.013 to 0.031 mg/sample. The corresponding PBZ concentrations for the three samples > LOQ ranged from 0.10 mg/m³ to 0.35 mg/m³.

Twelve PBZ samples were collected to evaluate for the presence of 2-butoxyethanol (butyl cellosolve). 2-butoxyethanol was not detected on any PBZ samples to the limit of detection of 0.0009 mg/sample.

Twelve PBZ samples were collected to evaluate for methyl ethyl ketone (MEK). MEK was not detected on any PBZ air samples to the LOD which was reported as 0.001 mg/sample.

Area air samples collected by marking a tree with several squirts of paint, then placing a sampling pump and thermal desorption tube immediately next to the painted area, confirmed the presence of propylene glycol and a mixture of mostly aliphatic hydrocarbons (stoddard solvent) in the C₉-C₁₂ range, and TMBs.

Biological Monitoring

Solvents or solvent metabolites were ND to the LODs in any of the urine samples which were analyzed. The LODs for MEK and MIBK were 0.10 milligrams per liter (mg/L). For 2-butoxyacetic acid (the metabolite for butyl cellosolve) the LOD was 60 milligrams per gram (mg/gm) creatinine. Ethylene glycol monobutyl ether creatinine was within the normal range of 300-3400 mg/L for adults for all urine samples. All urine samples were below

any ACGIH Biological Exposure Indices (BEI) for the solvents which were evaluated during this investigation.

DISCUSSION AND CONCLUSIONS

The purpose of this investigation was to evaluate Foresters' exposures to a waterborne formulation of tree marking paint. PBZ exposures measured in this investigation were below any occupational health criteria for the solvents evaluated, and were lower than measurements made in the preceding investigations where alkyd enamel paint was used. None of the irritant or CNS health effects reported by Foresters using alkyd enamel tree marking paint were reported by Foresters who used the waterborne paint formulation during this survey.

The only solvent measured above the LOQs in this investigation was total hydrocarbons (n=3) which were detected at trace concentrations, and propylene glycol (n=3) in concentrations of 0.32 mg/m³, 0.38 mg/m³, and 1.1 mg/m³.

PBZ exposures measured during three previous HHE surveys reveal that average concentrations of total hydrocarbons at: 2.7 mg/m³ on the Kisatchie National Forest (n=5); 4.4 mg/m³ Gifford Pinchot National Forest (n= 5); and 2.6 mg/m³ on the Wallowa-Whitman National Forest (n=21). Substitution of a reduced mineral spirit tree marking paint is believed to be the reason that PBZ exposures were reduced to ND, or in a few cases, trace concentrations during this HHE. The stoddard solvent content of the Niles brand blue alkyd enamel paint was reported on the material safety data sheet (MSDS) to be 34% by volume, the Niles brand blue waterborne formulation is reported to be 5% by volume. There were differences in this HHE compared to previous HHEs besides substitution of the waterborne paint. These factors include lower temperatures and higher RH. In this investigation three Foresters worked as a group compared to four or five Foresters during previous studies,

consequently less paint was applied to timber during this study (compared to the HHE on the Wallowa–Whitman) and less aerosol or vapor may have been emitted into the air in the immediate area where trees are marked. Decreased temperatures, increased RH, and less paint applied in the field imply that a worst–case scenario was not evaluated during this HHE. In fact, temperature and RH variations, differing crew sizes, and variation in the amount of paint applied are all representative variation which occur under normal field conditions. The factor most likely to influence hydrocarbon exposures more than reduced temperature, increased RH, or the total amounts of paint used, is using paint with a significantly reduced stoddard solvent content (34% compared to 5%). The six Foresters who applied waterborne paint during this survey (and on other occasions) did not report irritation, nausea, vomiting, or acute CNS symptoms as reported by Foresters using alkyd enamel paint during previous investigations. To date, some USFS crews report experiencing a sweet taste in their mouths after or during paint application. This is likely to be caused by propylene glycol. However, this exposure is unlikely to present health hazards to employees.

The results of this HHE indicate that product substitution was an appropriate and effective intervention to: (a) reduce employee solvent exposures as confirmed by PBZ air sampling and biological monitoring; and (b) reduce the health symptoms which were reported with the use of a higher percentage stoddard solvent–containing alkyd enamel paint. While the waterborne formulation still contains solvents, the primary solvent propylene glycol, is of a very low toxicity and a low volatility.

This study demonstrates that PBZ exposures to total hydrocarbons, toluene, MEK, MIBK, and tri–methyl benzene (the solvents of concern from a chronic low–level exposure perspective) are considerably lower than the LOD in most cases — compared to the alkyd enamel tree marking paint. Biological monitoring results of Foresters’ urine revealed an absence of the MEK, a solvent which was found in Foresters’ urine in two previous NIOSH studies where alkyd enamel tree marking was used.

RECOMMENDATIONS

NIOSH offers the following recommendations to the U.S. Forest Service based on the results of this and the other previous investigations.

1. The Forest Service should continue surveillance of employee health symptoms during field evaluation and use of the waterborne paint formulation. If it is determined that with increasing use, employees do not experience acute CNS health effects and irritation, the waterborne paint should replace the higher solvent alkyd enamel formulation.
2. NIOSH understands that the USFS is considering use of other waterborne paint formulations, one of which is a citrus solvent–based paint containing d–limonene. d–limonene is one of the main components of orange or lemon oils and is reported to enhance skin absorption of other chemicals.²² Use of d–limonene–containing paints could present possible risks from skin exposure if this paint contacts exposed skin.
3. As NIOSH previously recommended, the USFS should encourage employees to use the minimum number of trigger pulls required to mark a tree. One stump dot applied first, and two breast blazes applied second, may be helpful to avoid exposing employees’ breathing zone into paint mists while marking at ground–level. Employees should be made aware that paint mist contact on clothing can result in accumulated paint residues, where solvents can volatilize off the clothing resulting in low–level exposures in the employees breathing zone, even when an employee is not using paint to mark timber.
4. NIOSH recommends that USFS management continue to encourage employees to mark trees from an upwind position whenever possible. This may not always be feasible and can be difficult to do depending on terrain and other circumstances. However, employees should be informed of the rationale for the recommendation. It should be stressed to employees that limiting all exposures to paint mist and vapor is important, and in that regard,

employee suggestions and input into ways to accomplish this should be encouraged and recognized.

5. Employees should be encouraged to wear PPE in the field, especially safety glasses. During this survey some employees mentioned that certain brands of safety glasses caused vertigo, blurred vision, or headaches after a period of wearing. Many brands and styles of industrial eye protection (ANSI Z78 approved) are currently available, and quality between different brands of optics can vary. Employees should have access to distortion-free eye protection which does not cause complaints of vertigo or headaches.

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APPENDIX A



National Institute for Occupational Safety & Health

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July 27, 1998
HETA 98-0111

Mr. Frank Duran
Regional Measurement Specialist
Pacific Northwest Region
P.O. Box 3623
Portland, Oregon 97208

Dear Mr. Duran:

You asked that I prepare a synopsis of the results of health hazard evaluation (HHE) 98-0111 for the U.S. Forest Service Paint Committee meeting scheduled to take place during July 28-29, 1998, in Green Bay, Wisconsin. On February 11, 1998, you requested that the National Institute for Occupational Safety and Health (NIOSH) conduct a HHE to evaluate solvent exposures to Forest Service personnel who were applying a newly-formulated (water clean-up) tree marking paint. In the past, NIOSH has conducted four industrial hygiene timber marking HHEs in a number of national forests to evaluate exposures to timber markers when using traditional alkyd enamel formulations of tree marking paint. HHE 93-1035-2686, dated April, 1998, described the results of four NIOSH industrial hygiene studies which demonstrated that timber markers' exposures to solvents, dusts, and metals from tree marking paint were found to be below relevant occupational health criteria [e.g. permissible exposure limits (PELs), and recommended exposure limits (RELs)] for individual solvents, metals or dusts. Despite this, some Forest Service personnel reported health complaints consistent with exposure to petrochemical solvents when using standard formulations of tree marking paint.

HHE 98-0111 was performed May 19-21, 1998, on the Wallowa Whitman national forest at a timber sale outside of LaGrande, Oregon, to evaluate timber marker exposures associated with a new Niles Chemical Paint Company (water soluble) tree marking paint formulation. The paint that was used during the survey was N7039 Environmental Blue W/R tree marking paint manufactured by the Niles Chemical Paint Company. The material safety data sheet (MSDS) for this paint reported that the paint contained the following ingredients: propylene glycol 34% (all percentages hereafter are reported by weight), aluminum magnesium silicate (4%), mineral spirits (4%), alkyd resin (3%), odorless mineral spirits (2%), cobalt compounds (<1), and proprietary ingredients which are listed as "balance" on the MSDS.

As you know, NIOSH requested a paint formulation list from Niles Paint Company in a letter sent to Niles on March 10, 1998. The formulation list was not received by NIOSH prior to the date of the HHE. However, several bulk paint samples sent to NIOSH by the Forest Service enabled NIOSH to perform head space sampling and gas chromatography and mass spectroscopy (GC-MS) analysis on the paint samples to develop both an air sampling and biological monitoring sampling protocol. The major compounds detected

in bulk samples of paint analyzed by GC-MS were propylene glycol, butyl cellosolve (2-butoxyethanol) and a hydrocarbon mixture of C₉-C₁₂ alkanes, plus some alkyl benzenes. Additional compounds identified in head space samples included methanol, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), methyl propyl ketone (MPK), toluene, hexanal, xylene, propylene glycol methyl ether acetate, butyl acetate, methyl amyl ketone, and 2-methyl, 2-propanol.

During HHE 98-0111, NIOSH collected 48 personal breathing zone (PBZ) air samples. The PBZ samples were collected on six timber markers during two and one-half days of marking. Using NIOSH results from head space and GC-MS analysis of the bulk paint samples, PBZ exposures to the following chemicals were evaluated: propylene glycol, 2-butoxyethanol (butyl cellosolve), methyl ethyl ketone (MEK), total hydrocarbons, and toluene, trimethyl benzene, and methyl isobutyl ketone (MIBK).

In summary, during this investigation, exposures to solvents from the new formulation of timber marking paint was very low, in most cases the chemicals which were sampled for were reported as not detected (ND) or were detected at trace concentrations. Individual analyses for PBZ samples are listed below.

Total hydrocarbons

Of the 12 samples collected for total hydrocarbons, 9 (75%) were below the analytical limit of detection (LOD). Three samples (25%) were reported with trace amounts of total hydrocarbons (as stoddard solvent) which were between the LOD of 0.03 milligrams (mg) per sample and the LOQ of 0.09 mg per sample. NIOSH reports trace concentrations as non-numerical values because these data fall below the LOQ for the analytical method and therefore are non-numerical values. Toluene, total trimethyl benzenes, and methyl isobutyl ketone (MIBK) were all below the LOD for all of the samples. The LOD for toluene was 0.0003 mg/sample. The LODs for both total trimethyl benzene and methyl isobutyl ketone (MIBK) were 0.004 mg/sample.

Propylene Glycol

Of the 12 samples collected for propylene glycol, 9 (75%) were reported at a trace concentration. Three samples (25%) were reported with quantitative amounts of propylene glycol which was determined in a range of 0.10 parts per million (ppm) to 0.35 ppm. These values are based on a minimum detectable concentration (MDC) of 0.08 mg/m³ or 0.02 ppm. Neither NIOSH nor OSHA has a specific REL or a PEL for propylene glycol. The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a threshold limit value (TLV) of 50 ppm for ethylene glycol.

2-Butoxyethanol (Butyl Cellosolve)

The 12 samples collected for 2-Butoxyethanol (also referred to as the trade name butyl cellosolve), all were below the LOD (< 0.0009 mg/sample).

Methyl Ethyl Ketone (MEK)

The 12 samples collected for MEK all were below the LOD (< 0.001 mg/sample).

Biological Monitoring

The results of urinary biological monitoring for MEK and 2-Butoxyethanol (butyl cellosolve) have not been received from the analytical laboratory. E-mail correspondence from the NIOSH contract laboratory received by NIOSH on July 22, 1998, indicated that the laboratory was acquiring new analytical equipment. The letter explained that after standardization and performance measures are completed on the new equipment, the samples would be analyzed. These results will appear in the final report of the HHE.

The final HHE report will be sent to you when all analyses have been completed and the results are compiled. I appreciate your assistance, and specifically the assistance of the timber markers, the timber manager, and the Forest Service safety officer who provided NIOSH with assistance in this study. If you have any questions, please do not hesitate to contact me at (303) 236-6032 ext. 236

Sincerely yours,

Eric J. Esswein, MSPH, CIH
Industrial Hygienist
Industrial Hygiene Section
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October 23, 1998

Mr. Ronald F. Wilson
USDA Forest Service
Safety and Occupational Health Manager
1621 North Kent Street, RPE 900
Arlington, Virginia 22219

Dear Mr. Wilson:

This letter is in response to our conversation regarding product formulation specifications for tree marking paints used by the USFS. I received the email you sent to me which included the list of U.S. Navy specifications for solvent and metal percentages in Navy paint(s). The USFS is considering adopting new tree marking paint product formulations with the intent to continue development of paint(s) to minimize employee exposures to paint volatiles and still meet certain specifications, such as traceability, visibility and, durability. As I understood the discussion with you, Mr. Duran and Mr. Joe Zinni (employee union representative) the Forest Service is interested in NIOSH comment on tree marking paint formulations.

As you know NIOSH performed several health hazard evaluations (HETA 93-1035 and 98-0111) in several national forests across the U.S. I presented the air sampling results of a recent investigation (HETA 98-0111) at the paint committee on July 28-29, 1998. I also wrote an interim letter to the requestor, Mr. Duran providing him with results of air sampling from the investigation. HETA 98-0111 was conducted when employees used Niles Environmental blue water miscible tree marking paint. In the previous NIOSH investigations where the type I or type III alkyd enamel paints were used, personal breathing zone exposures (PBZ) to solvents and to metals were consistently below any occupational health criteria. In the most recent investigation, PZB samples were lower overall than any of the previous HHEs, in most cases the solvents which were sampled were not detected (ND) or were detected in trace or very low concentrations. It appears that product substitution was an effective measure to further reduce exposures to paint volatiles.

I reviewed the list of solvents from Table III in the US Navy specification. I would not recommend the USFS adopt the list in totality for several reasons; (1) It is not known whether the maximum limits (in percent by weight) listed in Table III were intended as pollution prevention concentrations (environmental air or water

pollution), or whether they were intended to limit inhalation exposures to paint constituents; (2) the list is not comprehensive for all hazardous materials present in paints (for example mineral spirits is not listed); and (3) percentage by weight of certain solvents in the Navy list (e.g. toluene, MEK and halogenated hydrocarbons) are in higher concentration than in the current formulation of water miscible paint according to the results reported March 30, 1998, by Calcoast Analytical. Based on the Calcoast results of bulk paint sampling and the air and bulk paint sampling results from HHE 98-0111 the following solvent percentages for blue water miscible paint should result in exposures (under similar conditions) no greater than those measured during the HHE conducted May 19-21, 1998.

Table 1

Chemical	% by weight (wet)	Comment
Benzene	<0.001 or <LOD	% determined by Calcoast analytical
Chlorinated solvents	<0.005 or <LOD	% determined by Calcoast analytical
C ₄ or higher alcohols	<0.004 or <LOD	% determined by Calcoast analytical
MEK	<0.001 or <LOD	% determined by Calcoast analytical
Toluene	0.008 or less	% determined by Calcoast analytical
Ethylene glycol ethers	<0.005 or <LOD	% determined by Calcoast analytical
MIBK	<0.005 or less	was not detected in PBZ samples HHE 98-0111
Propylene glycol	34% (per current formulation)	PBZ samples did not exceed 0.35 ppm
Formaldehyde	< limit of detection	
Methanol	as low as feasible	PBZ concentrations unknown as orange paint was not used
Total Mineral Spirits	6% or less (Type III odorless, Class C, aromatic content of 0-2.5%)	as per current formulation, amount detected in PBZ samples were <LOD or trace amounts

Results on NIOSH bulk paint analysis (head space and GC-MS) indicated that the major compounds detected in bulk samples of blue and orange paint were propylene glycol, butyl cellosolve (2-butoxyethanol) and a hydrocarbon mixture of C₉-C₁₂ alkanes, plus some alkyl benzenes. Additional compounds identified in head space samples included methanol (significant quantities in the orange paint), methyl ethyl ketone (MEK),

methyl isobutyl ketone (MIBK), methyl propyl ketone (MPK), toluene, hexanal, xylene, propylene glycol methyl ether acetate, butyl acetate, methyl amyl ketone, and 2-methyl, 2-propanol.

Since I have not received the product formulation for the blue and orange water miscible paint formulations, I cannot comment on chemicals which may be in the paint but were not detected by either the NIOSH analysis or the Calcoast analysis. If the product formulation can be made available to me I would be willing to review and provide you with comments. I know that there is concern surrounding the amount of toluene in the paint. Since toluene is an aromatic hydrocarbon, I recommend that the USFS specifies a commercial item description (CID) for mineral spirits according to ASTM D 235-95 Class C. This specification (see table 1 above) should limit toluene in the product formulation to less than two volume percentages (vol. %).

I hope this information will assist the paint committee regarding tree marking paint formulations. Please contact me at (303) 236-6032 ext. 236 if you have any questions regarding this letter.

Sincerely yours,

Eric J. Esswein, MSPH, CIH, R.S.
Industrial Hygienist
Industrial Hygiene Section
Hazard Evaluations and Technical
Assistance Branch
Division of Surveillance, Hazard
Evaluations and Field Studies

cc:
F. Duran
J. Zinni

For Information on Other
Occupational Safety and Health Concerns

Call NIOSH at:
1-800-35-NIOSH (356-4676)
or visit the NIOSH Homepage at:
<http://www.cdc.gov/niosh/homepage.html>



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